

# What Drives Osmosis?

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(Received: 4 January 1994; accepted in final form: 27 July 1994)

**Abstract.** This presentation claims that a fall in free energy, which is the rigorous thermodynamic criterion for a spontaneous change, cannot be the drive in osmotic processes. Our models and theories require the introduction of a parameter that explicitly represents structure in liquids, which until now has had no place in the thermodynamic description of solutions. This lack is surprising, when one remembers that experimental results from the broad range of fields of colloid, clay and biological sciences have clearly established the marked effect of solutes on the structural properties of water, globally called 'hydration phenomena'.

The introduction of such a parameter can help explain the direction in which energy flows during osmosis, which has been so puzzling to those of us interested in mechanism since the time of Pfeffer, more than a century ago. Further, elementary work cycles show, that changes in this parameter correspond to changes in the energy associated with solvent structure which can be used to produce useful work. The ability of osmotic systems to do work is familiar to all of us (indeed, a nuisance to many!), and is the basis of cytomechanics, i.e., the physical processes observed in the living cell. The fact that it still has no satisfactory explanation is clearly an urgent problem for us all.

**Key words:** Hydration, osmosis, osmotic work, random motion, water structure.

## 1. The Classical Theory

Over 100 years ago, Van't Hoff proposed his famous equation for osmotic pressure

$$\Pi = zkT, \quad (1)$$

where  $z$  is solute concentration in molecules per litre,  $k$  and  $T$  are Boltzmann's constant and temperature. Since then, physics has witnessed the success of the relativity and quantum theories and has even told us of events that happened at the beginning of time [1]. Yet we still do not know what the molecules of ordinary liquids do, when they produce an osmotic force.

In thermodynamic terms, equilibrium is reached when the free energy per mole or chemical potential,  $G$ , of solvent in the solution equals that in the pure solvent. The free energy is a function of the activity,  $a$ , of the solvent (whereby  $a = 1$  for the pure solvent) which upon integrating  $dG = \bar{V}dP$  leads to the familiar thermodynamic expression for the osmotic pressure

$$\Pi\bar{V} = P\bar{V} - P_0\bar{V} = -RT \ln a, \quad (2)$$

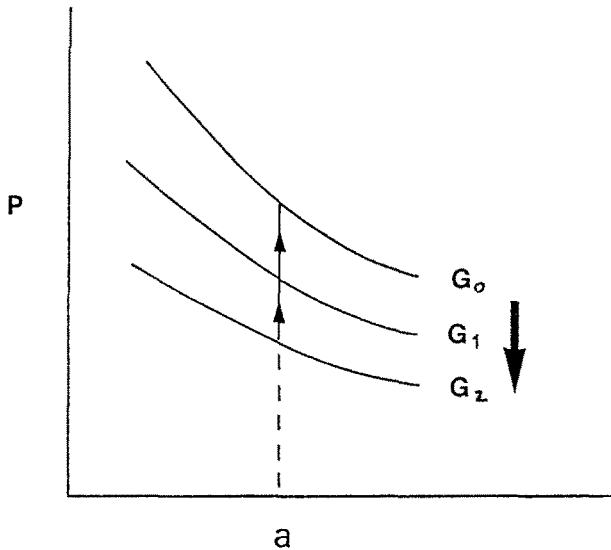


Fig. 1. The family of free energy curves showing pressure versus activity according to Equation (3). The large arrow on the right shows the direction of decreasing free energy. The rising arrow at a given activity represents the change in a natural system as it builds up osmotic pressure spontaneously.

where  $\bar{V}$ , the molar volume of the solvent, remains constant as usually assumed. If we include variation in  $\bar{V}$  with  $P$  and  $a$ , then Equation (2) becomes more complicated, however this does not affect the following argumentation. The free energy can be represented as the family of curves seen in Figure 1, showing the pressure on a solution as a function of its solvent activity.

$$G_0 : P = -(RT/\bar{V})\ln a + P_0, \quad (3)$$

$$G_1 : P = -(RT/\bar{V})\ln a + P_1. \quad (4)$$

$G_0$  corresponds to the pure solvent at ambient pressure  $P_0$  (usually atmospheric),  $G_1$  corresponds to the pure solvent, at a lower pressure  $P_1$ , etc. Figure 1 shows that the chemical potential of the solvent in a solution where the activity is, say  $a$ , increases when the pressure on that solution is increased. The upward arrow illustrates this change in a system as it moves towards equilibrium. The direction of this change means that the chemical potential is not the force underlying osmosis, because a spontaneous change is driven by a fall in chemical potential. What then does drive osmosis?

## 2. An Osmotic Machine

Figure 1 is reminiscent of the family of  $PV$  isotherms that describes the behaviour of gases. It therefore suggests a potential analogous to temperature, which is the

potential that drives spontaneous heat flow. Thus we now introduce an intensive property, like temperature, which characterises solutions. This property, denoted here by  $\sigma$ , defines the level of structural energy, analogous to thermal energy, whereby for two systems in contact, energy will flow from that where the structural parameter,  $\sigma$ , is higher into that where  $\sigma$  is lower.

To examine this potential we recall how a temperature difference drives a heat machine operating between the higher and lower temperatures  $T_0$  and  $T_1$  shown in Figure 2. The adiabatic steps of Carnot's original cycle (B to C and D to A), where work is done to change the temperature, have been modified to steps at constant volume where no work is done. From A to B, the machine which is a cylinder containing  $N$  molecules of a perfect gas behind a piston exerting pressure  $P$ , expands down the isotherm  $T_0$ , while absorbing the necessary heat from a source at temperature  $T_0$ . From B to C, it is put in contact with a series of sources in succession, each having a slightly lower temperature than the preceding one, until the temperature falls to  $T_1$ . During this step, heat flows out of the gas without a change in volume, causing its temperature to drop. From C to D and D to A the steps are reversed, completing the cycle. The work done by the machine is the difference in areas under the isotherms,

$$W = Nk(T_0 - T_1)\ln(V_2/V_1), \quad (5)$$

which is the same as that obtained during Carnot's original cycle.

In the case of the osmotic machine, the walls transmit solvent rather than heat, i.e. they function as semipermeable membranes. The cylinder contains  $N$  solute molecules dissolved in an ideal solution of concentration  $z = N/V$ . The piston exerts the equilibrium pressure  $P$  on this solution, which is the pressure in the surrounding source solution,  $P_0$  (usually atmospheric), plus the osmotic pressure,  $\Pi = P - P_0$ . A series of ideal solutions, each with an incremental increase in solute concentration over the preceding one, act as the external source solutions, in the same way as we have the heat sources at decreasing temperatures in the Carnot cycle. They range from the pure solvent with the highest structural parameter,  $\sigma_0$ , down to a solution of concentration  $z_1$  with structural parameter  $\sigma_1$ .

At A in Figure 3, the solution inside is in equilibrium with the pure solvent outside, so the value of the structural parameter is  $\sigma_0$  both inside and outside the machine. From A to B it remains in contact with the pure solvent which enters the machine diluting the solution inside, while it expands down the  $\sigma_0$  'isotherm'. During this step, the osmotic pressure falls because of the corresponding decrease in the concentration inside. From B to C, the machine is put in contact (immersed in) and equilibrated with the series of solutions of decreasing structural parameter in succession, until its value falls to  $\sigma_1$ . As in Figure 2, during this step the volume remains constant and so there is no work done. However, the solvent medium is continuous, connecting the inside and outside solutions, and so structural energy flows outwards establishing osmotic equilibrium each time causing the drop in  $\sigma$ . The step C to D reverses the step A to B, but this time the machine is in contact

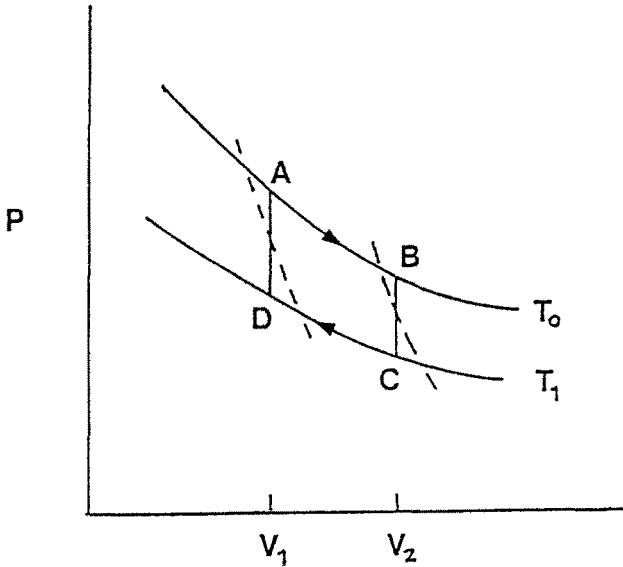


Fig. 2. The Carnot cycle. The adiabatic steps (dashed lines) of the classical cycle have been replaced by steps at constant volume B to C and D to A. During these steps the machine must be equilibrated with an infinite series of heat sources covering the temperature range  $T_0$  to  $T_1$ .

with the solution having the lowest value of the structural parameter,  $\sigma_1$ . D to A reverses B to C completing the cycle.

During the cycle, the solute concentration of the inside solution is kept higher than that of the outside source solutions. This ensures that  $\Pi$  remains positive, i.e. that  $P$  does not fall below  $P_0$ , although this restriction is not necessary. If  $V$  is continuously increased, then the inside solution becomes indefinitely diluted and approaches the composition of the pure solvent. For the expansion A to B, where the solution is in any case in contact with the pure solvent, this means that the point B would move further down the  $\sigma_0$  'isotherm' approaching the ambient pressure  $P_0$  asymptotically. If the machine expands while in equilibrium with the solution  $\sigma_1$ , on the other hand, the pressure must cross  $P_0$  at that volume where  $z = z_1$ . Now  $\Pi$  becomes negative, i.e. the piston must be pulled rather than pushed, because this  $\sigma_1$  'isotherm' approaches the pressure  $P_1$  asymptotically. This is the pressure of the pure solvent, now on the inside, in equilibrium with a solution of concentration  $z_1$  at pressure  $P_0$  on the outside, as was established experimentally by Mauro [2],

$$\Pi = P_1 - P_0. \quad (6)$$

Thus these 'structure isotherms' are analogous to temperature isotherms, except that the asymptotic value on the  $V$ -axis is not set by zero gas concentration  $P = 0$ , but by zero solute concentration, i.e., by the osmotic pressure at infinite dilution. Hence, they take the form

$$P = zkT\sigma_0 + P_0, \quad (7)$$

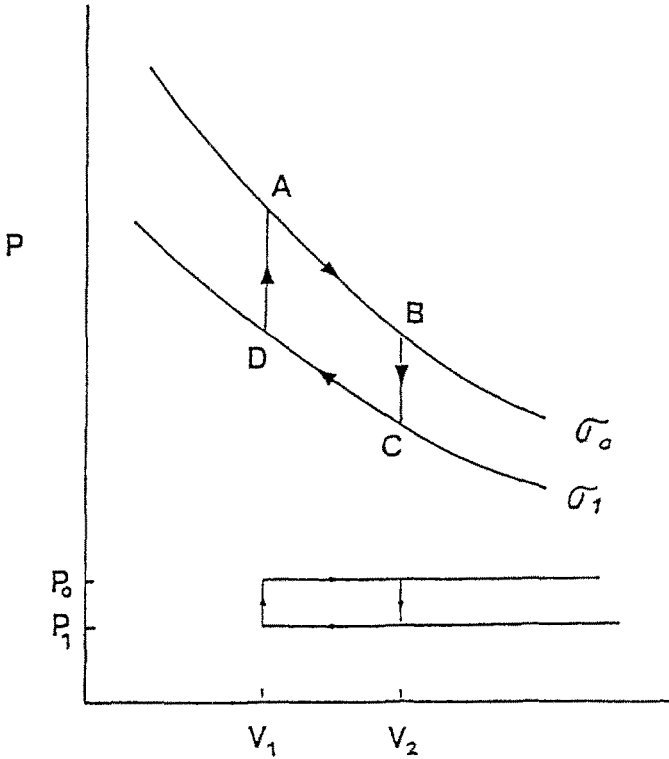


Fig. 3. The osmotic machine. The curves labelled  $\sigma_0$  and  $\sigma_1$  are  $PV$  hyperbolae analogous to the  $T_0$  and  $T_1$  isotherms in Figure 2, whereby  $\sigma_0$  and  $\sigma_1$  are asymptotic to their minimum pressures  $P_0$  and  $P_1$  respectively. Equation (9) shows that part of the total area of the Carnot cycle ABCD is equal to the area of the rectangular cycle shown between the asymptotes.

$$P = zkT\sigma_1 + P_1. \tag{8}$$

As in Figure 2, the work done by one cycle of the osmotic machine in Figure 3 equals the difference in areas under the isotherms.

$$W = NkT(\sigma_0 - \sigma_1)\ln(V_2/V_1) + (P_0 - P_1)(V_2 - V_1). \tag{9}$$

Van't Hoff's equation describes behaviour under ideal conditions, at infinite dilution and vanishingly small osmotic pressure, just as the gas law expresses ideal behaviour. Thus, we can define a scale to measure the structural parameter in the same way as the ideal gas temperature scale was set up to measure temperature. Indeed, the device called the constant volume thermometer, which measures pressure, was developed on the principle that the pressure of a gas is a direct measure of its temperature ( $T_1/T_2 = P_1/P_2$ ). Likewise, from Equations (7) and (8) we can define an ideal structural parameter scale according to

$$\sigma_1/\sigma_0 = (P - P_1)/\Pi. \tag{10}$$

This means that the value of  $\sigma$  in a solution, compared to that in the pure solvent, equals the ratio of the difference in the pressure developed by a second solution in contact with it and that developed by the pure solvent in contact with it (this latter being smaller than  $P_0$ , see Equation (6)), to the osmotic pressure of the second solution. Although this expression gives the variation in the parameter, it does not give actual values. In the next section this further step is made possible, since there the value of  $\sigma_0$  is anchored at unity.

### 3. Interpretation

The proposal of a parameter,  $\sigma$ , to explain osmotic effects has been introduced on the basis of arguments on the macroscopic level only. However, the main aim for those of us interested in mechanism, is to construct a model in terms of events on the molecular level. The simplest view would be that  $\sigma$  is a factor that measures to what extent solvent structure becomes modified or 'degraded' by the introduction of foreign solutes. Its maximum value is  $\sigma_0 = 1$ , because then Equation (7), which describes a solution in equilibrium with pure solvent, becomes identical to Van't Hoff's equation

$$\Pi = z k T. \quad (1)$$

We interpret a fall in temperature as a decrease in molecular energies, especially bond vibrations in the case of liquids. Then using the analogy with temperature once more, a decrease in  $\sigma$  would mean a lower energy of a multimolecular complex seen as a vibrational unit. A foreign molecule disrupts the solvent-solvent interactions, interfering with their geometry and thus breaking down the extent of their co-operative influence. It is this large scale grouping of intermolecular bonds that is affected, not individual inter- and intramolecular bonds, whose thermal energy  $kT$  is not affected, since  $T$  does not change.

If we imagine a single bond to be a vibrating spring, we can interpret  $k$  as a type of spring constant and  $T$  as the variable which indicates how much energy the spring possesses at a particular vibration mode. Now, a co-operative group of intermolecular bonds which vibrates as a unit, can also be viewed as a spring. Each of these structural units is supplied with thermal energy at the same level  $T$ , whether it is in a solution or the pure solvent. But in the case of the solution, the strength of the spring has been lowered compared to the pure solvent, and so in solutions,  $\sigma$  takes values less than 1. In other words, solvent structures possess lower energy in solutions than in pure solvent under the same conditions of temperature and pressure.

### 4. Discussion

As we have seen, the classical theory does not explain the driving force in osmotic processes, nor does it give us an indication of molecular mechanism. In the preceding Interpretation section, the alternative concept of co-operative structuring was

then put forward as the mechanism underlying osmosis. But how could structuring explain how liquid molecules flow against pressure, when classical thermal motion cannot?

I have proposed earlier [3] that clusters form in liquids as the result of co-operative interactions between molecules. These aggregates do not appear and disappear spontaneously at random, but travel through the medium producing a wave pattern as a result of their long-range influence. In this wave-cluster model the size of a cluster is given by the volume of a wave unit,  $u_0$ , the region of space determined by the wavelength, which obeys the gas law [4].

$$P_0 u_0 = kT. \quad (11)$$

The intermolecular forces hold a cluster together like a giant 3D molecule, because the molecules are momentarily bonded to one another. Thus a cluster is internally under tension, not pressure. In this picture, it is easy to see how a molecule in the neighbourhood can be pulled into a cluster and become part of its large structure. Because co-operative effects are long-range, clusters formed by strong bonding exert a pull on molecules in those clusters where interactions are weaker. We now have a mechanism for the action of a concerted, directed, mechanical force operating within liquids. It is just such a force that is needed to explain osmosis. (For pictorial representations see [4] and [8]).

The effect of solute on solvent was interpreted in the previous section, as the breaking up of clusters, reducing their size and energy, so that in solution

$$P_0 u = \sigma kT, \quad (12)$$

where  $u < u_0$  and  $\sigma < 1$ . When solvent and solution are in contact, say across a membrane, the clusters exchange energies as a result of the co-operative wave motion, and there is a net energy flow from the energy-rich clusters of the solvent into the smaller clusters of the solution. This increases  $\sigma$  and thus the tensile strength of the intermolecular bonds, so that the smaller clusters can pull solvent across the membrane increasing the pressure on the solution side. At equilibrium,  $P$  has become high enough to counteract the pull of the smaller clusters and equalise flow. At this point, the energy of the smaller solution clusters equals that of the pure solvent clusters

$$Pu = P_0 u_0 = kT. \quad (13)$$

This equation can be rearranged to give

$$P - P_0 = \left( \frac{1}{u} - \frac{1}{u_0} \right) P_0 u_0, \quad (14)$$

or

$$\Pi = \left( \frac{1}{u} - \frac{1}{u_0} \right) kT. \quad (15)$$

The introduction of solutes increased the concentration of clusters from  $1/u_0$  to  $1/u$ . It was argued elsewhere that this increase is equal to the concentration of solute molecules, because it represents the increase in the number of nodes in the wave motion [4].

$$z = \frac{1}{u} - \frac{1}{u_0}. \quad (16)$$

It then follows that Equation (15) is identical to Equation (1). Thus, the mechanism based on the wave-cluster model of dynamic structures formed by intermolecular tension leads to Van't Hoff's well known expression describing equilibrium.

An important feature of the model is that, as the clusters exchange energy, they are able to do work. Clusters enter the osmotic machine (Figure 3) from the solvent with energy  $kT$  and leave by transfer to a solution with energy  $\sigma kT$ . The work done resembles that done by a gas in the Carnot cycle (Equation 5), although there is the additional term,  $(P_0 - P_1)(V_2 - V_1)$ , due to the different levels of pressure of the base lines at infinite dilution,  $P_0$  and  $P_1$ . To my knowledge, there is no published interpretation of the energy source for the osmotic machine, whether in terms of classical thermodynamics or modern statistical theories of liquids. In the accepted view the energy is supplied by free energy, however, the meaning of this in molecular terms is never presented, and in any case, this free energy would not be supplied in a spontaneous change, as shown above (Figure 1).

In the wave-cluster model the energy source is clear. Energy for work is supplied by the fall in structural energy of a cluster, just as in a heat machine energy is supplied by a temperature drop. This result reinforces the concept of a cluster as a vibrating wave unit or spring. In the pure solvent the spring is strongest, while in a solution it is weaker, or less energetic, unit for unit. The energies belong to co-operative aggregates of molecules acting as large individual entities. They are not the sum of separate energies belonging to separate molecules, i.e. they are not random thermal energies.

Exciting new developments in the field of quantum physics support this picture. Application of quantum theory to the liquid state predicts wave-particles of de Broglie wavelength in the same nm range as the wave clusters [5]. Independent investigations into the application of quantum field theory to biological systems also indicate the existence of macroscopic wave-particles in cell water [6], and recent developments in this theory predict spontaneous 'creation of long-range correlation waves' resulting from the ordering influence of cytoskeletal filaments on intracellular water [7]. The interaction of water with biological structures such as membranes and protein filaments generates the ordering of this hydration water responsible for its solid-like state (gelation) and the hydration force [8]. The importance of this hydration state is highlighted by the proposal that it is the basis of quantum coherence, which carries the propagation of photons along microtubules thus allowing rapid information processing at the subcellular level [9]. This proposal has recently been taken up by many workers and developed into models of



brain mechanisms and even consciousness (see articles in ‘Towards a Scientific Basis for Consciousness’, Hameroff S.R., Kaszmiak A.W., Scott A.C. (eds), MIT Press, 1995, in press, by Hagan, Yasue and Watterson).

## 5. Conclusion

This work presents a new molecular mechanism to explain osmotic processes. Beneath the macroscopic phenomenon of pressure, intermolecular tension operates, and this tension determines the direction of liquid flow. It also explains how systems can swell against imposed pressure [10], and why a gel is held together like a solid [8]. This tension gives rise to cluster formation in liquids, because at any instant, temporary intermolecular bonds hold a grouping of molecules together like a single giant 3D molecule. However, the presence of solutes interferes with this extensive bonding, thus lowering the strength of these structural forces. In other words, clusters in solutions have lower cohesive energy than those in pure solvents. Energy differences give rise to energy flows. It is this structural, and not random, energy that underlies osmotic and hydration phenomena.

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